

PATENT
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UNITED STATES PATENT APPLICATION

of

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for

AGRICULTURAL FORMULATION

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RELATED APPLICATIONS

This application claims benefit to U.S. Provisional Serial No. 60/270,311 filed February 21, 2001 which is incorporated by reference in its entirety for all useful purposes.

BACKGROUND OF THE INVENTION

Many agricultural formulations contain water-soluble salts. These salts, often alkylamine salts, are generally not as active as their acid equivalents. For example, 2,4-Dichlorophenoxyacetic acid (2,4-D acid) is known to be more herbicidally active than the dimethylamine salt of 2, 4-D. However, 2, 4-D acid is not soluble in water. Solvents used to formulate 2,4-D acid are known to be phytotoxic to plants and enhance herbicide volatility and subsequent drift to non-target areas. In another example, boron is known to be available to plants only in the boric acid form. However, boric acid is only soluble at relatively low concentrations in water, while the Monoethanolamine salt of boric acid is known to be much more soluble.

U.S. Pat. No. 4,332,609 issued to Ott, which is incorporated by reference in its entirety, discusses the means of producing just such a water-soluble concentrate of boric acid and Monoethanolamine. The disadvantage is that the plants must convert this boric acid Monoethanolamine complex to boric acid in order to use it. Furthermore, boron is often applied in conjunction with a variety of agricultural pesticides that are subject to degradation at high pH ranges. The boric acid Monoethanolamine salt produces high pH solutions and therefore is detrimental to many pesticides.

U.S. Patent No. 5,877,112 assigned to Helena Chemical Company, which is incorporated by reference in its entirety, describes a composition containing

- (a) at least one acid ester surfactant (phosphate ester surfactants)
- (b) at least one amine containing surfactant
- (c) and at least one water soluble agricultural chemical.

The formulation is expensive, largely because of the addition of phosphate ester surfactants. It would be beneficial if there were alternative, less expensive ways of obtaining formulation stability than using phosphate esters. Furthermore, the phosphate ester surfactants contribute to the eye irritation severity of the overall formulation.

U.S. Pat. No. 5,389,598 assigned to Monsanto Company, which is incorporated by reference in its entirety, describes a storage stable aqueous composition containing

- (a) water-soluble pesticide or plant growth modifying agent,
- (b) an alkylamine surfactant,
- (c) a C₆-C₂₂ saturated or unsaturated alkyl monocarboxylic or dicarboxylic acid
- (d) and water.

5 The third ingredient (c) C₆-C₂₂ saturated or unsaturated alkyl monocarboxylic or dicarboxylic acid is essential and must be present in a ratio alkoxylated alkylamine surfactant to C₆-C₂₂ saturated alkyl mono or dicarboxylic acid from at least about 2:1. The ratio of glyphosate to carboxylic acid is from about 10:1 (a) to about 100:1 and preferably about 10:1 to 40:1. Fattyamine ethoxylates have been known to be used in agricultural formulations in the past.

10 Specifically, tallowamine ethoxylate surfactant is known to enhance glyphosate activity and translocation.

WO 00/41567 describes the use of an adjuvant composition containing

- (a) polyoxyalkylene aliphatic amine
- (b) an eye irritation reducing compound (carboxylic acid)
- 15 (c) mixture of polyhydric alcohols preferably a trihydric alcohol and at least one diol such as ethylene glycol or propylene glycol.

The carboxylic acid is present in an amount from about 0.05 to about 5 wt.% of the adjuvant. When the adjuvant is used with glyphosate, the amount of carboxylic acid in the formulation is from about 0.2 to about 0.4% wt. %.

20 We have found that the invention without a polyhydric alcohol or a mixture of polyhydric alcohols. Furthermore, the invention can be practiced with an eye irritation amount of carboxylic acid which is the opposite taught by WO 00/41567.

SUMMARY OF THE INVENTION

25 The present invention is a composition comprising

- (a) a carboxylic acid or phosphorous containing acid providing that the phosphorous containing acid is not a glyphosate,
- (b) an amine containing surfactant,
- 30 (c) at least one water soluble agricultural chemical

with the proviso that the composition contains less than 3 percent by weight of phosphate ester surfactant. It is more preferable, that there is less than about 1 percent by weight of phosphate ester surfactant and most preferable there is no phosphate ester surfactant present. We have found that the invention can work without a polyhydric alcohol or a mixture of polyhydric alcohols. Furthermore, the invention can be practiced with an eye irritation amount of carboxylic acid. The amount of the carboxylic acid used is preferably an eye irritating amount greater which would be greater than 0.4 wt. %. More preferably, the amount of the carboxylic acid is at least 1%, and even more preferably at least 4 wt. % and even more preferably at least 6 wt.% and most preferably at least 7 wt. %.

The present invention is also a homogenous agricultural liquid composition containing at least (a) a carboxylic acid or phosphorus containing acid, (b) an amine containing surfactant, preferably a fatty amine ethoxylate surfactant, (c) and at least one other agricultural chemical without substantially no or no acid ester surfactants such as phosphate ester surfactants.

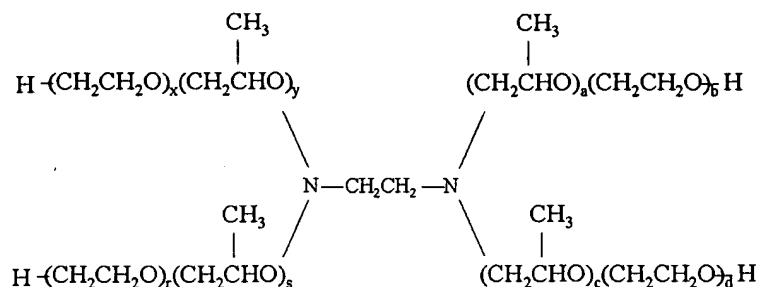
The agricultural chemical referred to herein, can used in agricultural or non-agricultural applications. The agricultural applications include, but are not limited to pesticide, fertilizer, or plant growth regulators. The non-agricultural applications include, but are not limited to forestry, aquatics, right of way (such as the areas along roads or medians), turf (such as lawns, golf courses etc.) ornamental (such as plants for their beauty) or municipal (parks, school, open land, etc).

The present invention works with substantially no or no phosphate ester surfactant. The preferred embodiment can have a weight/weight ratio of glyphosate to carboxylic acid less than about 10:1 and more preferably less 8:1 and most preferably less than about 7:1. The glyphosate and carboxylic acid are most preferably in a weight/weight ratio of glyphosate to carboxylic acid in a 8: 1 to about 2:1.

A further embodiment of the invention is a composition comprising:

(a) a phosphorous containing acid providing that the phosphorous containing acid is not a glyphosate,

(b) an amine containing surfactant of the formula:



where x,y,a,b,c,d,r, and s are independently a number from 0-100, with the proviso that the sum of a+b+c+d+r+s+x+y must be at least 4,

(c) at least one water soluble agricultural chemical

5 with the proviso that the composition contains less than 3 percent by weight of phosphate ester surfactant.

Optionally, other surfactants or formulation aids can be added. The formulation can have a pH of less than about 7. It is also possible to add a buffering agent to further decrease the pH of the composition.

Preferably, if a carboxylic acid is used, the acid is a monocarboxylic acid, a dicarboxylic acid and a tricarboxylic acid. The acid is formic acid, acetic acid, propionic acid, butyric acid, valeric acid, oxalic acid, malonic acid, succinic acid, glutaric acid, citric acid and phosphoric acid, preferably, citric acid. If a phosphorus containing acid is used, preferably it is phosphoric acid or phosphorous acid. Preferably the amine containing surfactant is a fatty amine and most preferably a tallowamine ethoxylate. The composition allows water-soluble salts of agricultural chemicals to remain stable and soluble at lower than normal pH ranges.

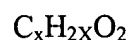
20 DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT

It has been surprisingly discovered that a wide range of water soluble compounds can be stabilized at lower than normal pH ranges using a combination of phosphorus containing acids or monocarboxylic, dicarboxylic or tricarboxylic acids and amine containing surfactants such as, but not limited to fatty amine ethoxylates.

The phosphorus containing acids are for the purposes of this patent, considered non-surfactants. That is, the surface tension for these acids is greater than 60 dynes/m as measured by a Du Nuoy Surface Tensiometer at a concentration of 1-10%.

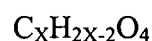
Preferably, the phosphorus containing acid is phosphoric acid or phosphorous acid. The commercial grades of these acids contain anywhere from 50-85% pure H_3PO_4 or H_3PO_3 .

The monocarboxylic acids are of the formula



wherein x is 1 to 5.

The dicarboxylic acids are of the formula

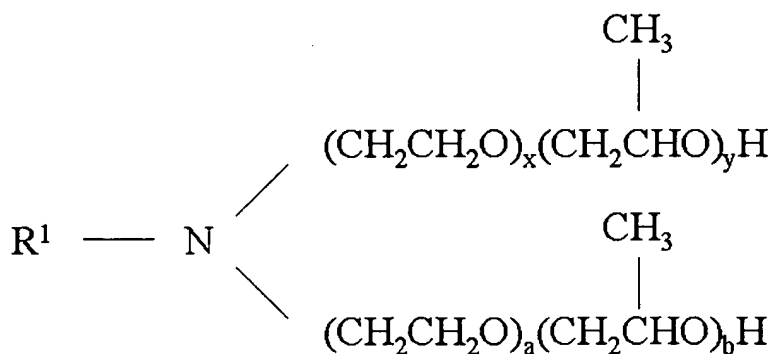


wherein x is 2 to 5.

Any tricarboxylic acid is effective.

The amine containing surfactants can be, but are not limited to fatty amine alkoxyates or block copolymers derived from the sequential addition of ethylene oxide and optionally propylene oxide to form ethylenediamines.

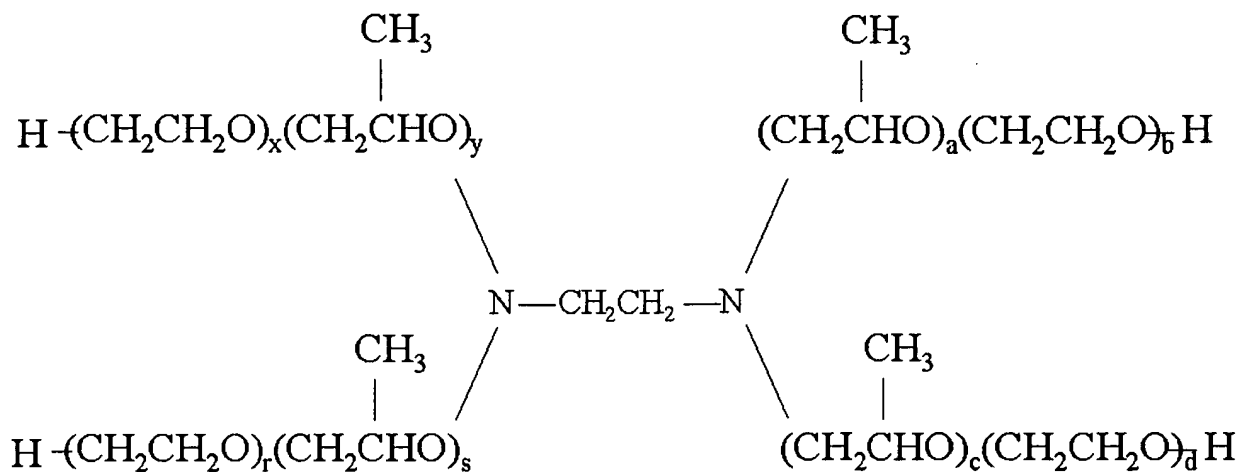
The fatty amine alkoxyates are of the formula:



wherein R^1 is a C_8 - C_{22} alkyl group,

x, y, a, and b are identical or different and are a number from 0 to 100 with the proviso that x+y+z+b is at least 2. The most preferred fatty amine alkoxyate surfactant is a tallowamine ethoxyate. The fatty amine containing surfactant can be present in an amount from about 1 to about 99%. Preferably, the fatty amine containing surfactant is present in an amount sufficient to enhance the efficacy of the crop protection chemicals.

The block copolymer derived from the sequential addition of ethylene oxide and propylene oxide to ethylenediamine is of the formula:



where x, y, a, b, c, d, r, and s are identical or different are a number from 0 to 100, with the proviso that the sum a+b+c+d+r+s+x+y must be at least 2. The most preferred fatty amine alkoxyate surfactant is a tallowamine ethoxylate. The fatty amine containing surfactant can be present in an amount from about 1 to about 99%. Preferably, the fatty amine containing surfactant is present in an amount sufficient to enhance the efficacy of the crop protection chemicals.

The agricultural chemical can be a fertilizer containing boron, zinc, copper, iron, blends of nitrogen phosphorous and potash or mixtures thereof. The fertilizer can be ammonia sulfate, an ammonia salt of a carboxylic acid, mono- or di-potassium phosphate, a micronutrient, ammonia nitrate, urea, ammonia citrate or ammonia acetate.

The agricultural chemical can be a crop protecting chemical such as, but not limited to a herbicide, insecticide or fungicide. The herbicide can be, but not limited to, dimethylamine (DMA) salt of 2,4-dichlorophenoxyacetic acid, DMA salt of dicamba, sodium salt of dicamba, isopropylamine (IPA) salt of glyphosate, IPA salt of 2,4-dichlorophenoxyacetic acid, sodium salt of acifluorfen, sodium-salt of bentazon, sodium salt of imazethapyr, ammonium salt of imazaquin, IPA salt of imazapyr, sodium salt of asulam or mixtures thereof. The agricultural chemical can be present in an amount from about 1 to about 99%.

The composition can contain micronutrients such as, but not limited to a water soluble salt of boron, iron, manganese, magnesium, copper or zinc. In example I, Ott's patented composition of a monoethanolamine salt of boric acid is further unexpectedly improved by using a blend of phosphate ester and an amine surfactant such as tallowamine ethoxylate.

5 The agricultural formulation can also contain additional surfactants. The preferred additional surfactants include, but are not limited to:

- a) sorbitan fatty acid ester,
- b) polyethoxylated derivative of a sorbitan fatty acid ester,
- 10 c) fatty alkanolamides
- e) silicone surfactants
- f) ethoxylated fatty
- g) alkyl ethoxylates
- h) alkylphenol
- 5 i) polypropylene glycols
- j) tristyrylphenol alkoxylates,
- k) amine ethoxylates
- l) N-Acyl Sarcosines and Sodium N-Acyl Sarcosinates,
- m) alkylaryl polyethoxy carboxylate ester,
- 20 n) tristyrylphenol alkoxylate carboxylate esters,
- o) alkylpolyglucosides.

Additionally, buffering agents can be added to the composition to further reduce the pH. The buffering agents include, but are not limited to,

- 25
- a) glutaric acid,
 - b) gluconic acid,
 - c) lactic acid,
 - d) glycolic acid,
 - 30 e) acrylic acid,
 - f) carboxylated alcohol ethoxylate,

- g) ethoxylated alkylphenol carboxylate esters;
- h) tristyrylphenol alkoxylate phosphate esters;
- i) tristyrylphenol alkoxylate carboxylate esters; and
- j) fatty acids and blends thereof and

5

The formulation can optionally contain water insoluble agricultural chemicals, such as but not limited to, pesticides. The pesticides can be, but are not limited to ester of dichlorophenoxyacetic acid, trifluralin, pendimethalin, propanil, atrazine, benefin, chloroimuron, linuron, alachlor, metalochlor or mixtures thereof.

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Furthermore the agricultural formulation can have a surface tension of less than 60 dynes as measured by the Du Nuoy Surface Tensiometer at a concentration of 1-10%.

The formulation is made by mixing all the ingredients together. Other optional ingredients include but are not limited to dyes, thickeners, anti-corrosion agent, anti-caking agents, stabilizers, gel inhibitors, anti-freezes, anti-foam agents, mixtures thereof and the like.

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The following examples are listed to help illustrate the advantage of the new agricultural formulation. All the examples are described in a percent by weight basis.

EXAMPLE 1

20

Ingredients	% in formula
Monoethanolamine salt of boric acid	80.0
Tallowamine ethoxylate surfactant	10.0
Citric acid	10.0

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The improvement of this formula is in the resulting pH of the composition. The monoethanolamine salt of boric acid has a pH of 9.0 on its own. The composition of Example 1 has a pH of about 7.0. It is generally acknowledged in most agricultural applications that plants can only use boron in it's acidic form.

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The patented composition can contain pesticides such as the dimethylamine salt of 2,4-Dichlorophenoxyacetic acid (2,4-D Amine). In Example 2, the water-soluble agricultural

chemical is the dimethylamine salt of 2,4-D, the tricarboxylic acid is citric acid, the amine containing surfactant is tallowamine ethoxylate, and the other surfactants are wetting agents. The resulting composition has a pH of about 6.0, as opposed to conventional dimethylamine salt of 2,4-D formulations which have a pH of about 8.5. The formulation in Example 2 produced a nice clear solution.

EXAMPLE 2

Ingredients	% in formula
Dimethylamine salt of 2,4-D	69.90
Tallowamine ethoxylate surfactant	13.40
Citric acid	10.40
Alcohol ethoxylate surfactant	2.80
Water	3.50

In Example 3, the water-soluble agricultural chemical is the dimethylamine salt of 2,4-D, the carboxylic acid is acetic acid, the amine containing surfactant is tallowamine ethoxylate, and the other surfactants are alcohol ethoxylates.

EXAMPLE 3

Ingredients	% in formula
Dimethylamine salt of 2,4-D	69.90
Tallowamine ethoxylate surfactant	13.40
Acetic acid (glacial)	10.40
Alcohol ethoxylate surfactant	2.80
Water	3.50

In Example 4, the water-soluble agricultural chemical is the dimethylamine salt of dicamba, the tricarboxylic acid is citric acid, the amine containing surfactant is tallowamine ethoxylate, and the other surfactants are wetting agents.

EXAMPLE 4

Ingredients	% in formula
Dimethylamine salt of dicamba	69.90
Tallowamine ethoxylate surfactant	13.40
Citric acid	10.40
Alcohol ethoxylate surfactant	2.80
Water	3.50

In Example 5, the water-soluble agricultural chemical is the dimethylamine salt of 2,4-D, the carboxylic acid is propionic acid, the amine containing surfactant is tallowamine ethoxylate, and the other surfactants are wetting agents.

EXAMPLE 5

Ingredients	% in formula
Dimethylamine salt of 2,4-D	69.90
Tallowamine ethoxylate surfactant	13.40
Propionic acid	10.40
Alcohol ethoxylate surfactant	2.80
Water	3.50

In Example 6, the water-soluble agricultural chemical is the isopropylamine salt of glyphosate, the tricarboxylic acid is citric acid, the amine containing surfactant is tallowamine ethoxylate, and the other surfactants are wetting agents.

EXAMPLE 6

Ingredients	% in formula
Isopropylamine salt of glyphosate	69.90
Tallowamine ethoxylate surfactant	13.40
Citric acid	10.40
Alcohol ethoxylate surfactant	2.80
Water	3.50

In Example 7, the water-soluble agricultural chemical is the isopropylamine salt of glyphosate, the carboxylic acid is acetic acid, the amine containing surfactant is tallowamine ethoxylate.

EXAMPLE 7

Ingredients	% in formula
Isopropylamine salt of glyphosate	69.90
Tallowamine ethoxylate surfactant	13.40
Acetic acid	10.40
Water	6.30

In Example 8, the water-soluble agricultural chemical is the dimethylamine salt of 2,4-D, the carboxylic acid is ascorbic acid, the amine containing surfactant is a block copolymer of EO and PO forming an ethylenediamine, and the other surfactants are wetting agents.

EXAMPLE 8

Ingredients	% in formula
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	Dimethylamine salt of 2,4-D	69.90
	Tallowamine ethoxylate surfactant	13.40
	Ascorbic acid	10.40
	Alcohol ethoxylate surfactant	2.80
5	Water	3.50

The inventive composition can be used in a method of controlling vegetation by adding the inventive composition to foliage of plants. Further, the inventive composition can be used in a method of promoting plant growth and/or eliminating the damage caused by insects by adding the inventive composition to foliage of plants. This invention would normally be introduced into some carrier such as water, fertilizer or oil.

The following patents and reference, which include several ingredients that can be used according to this invention, are incorporated by reference in its entirety for all useful purposes:

US05741502 Homogeneous, essentially nonaqueous adjuvant compositions with buffering capability

US05725630 Dry granular fertilizer blend and a method of fertilizing plants

US05580567 Homogeneous, essentially nonaqueous adjuvant compositions with buffering capability

US05393791 Homogeneous, essentially nonaqueous adjuvant compositions with buffering capability

US05234919 Water soluble, highly active dimethoate formulations in an alcohol/ester solvent system

US05178795 Homogeneous, essentially nonaqueous adjuvant compositions with buffering capability

US05906961 Alkanolamide spreader-sticker surfactant combination

US05877112 Agricultural formulation

All the references discussed in this application are incorporated by reference in their entirety for all useful purposes.

While there is shown and described certain specific structures embodying the invention, it will be manifest to those skilled in the art that various modifications and rearrangements of the parts may be made without departing from the spirit and scope of the underlying inventive concept and that the same is not limited to the particular forms herein shown and described.

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